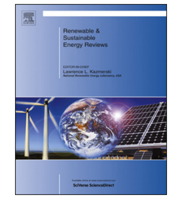
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An overview on the production of bio-methanol as potential renewable energy

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ABSTRACT

The depletion of the fossil fuel supply and the environmental pollution caused by fossil fuel combustion have become major worldwide problems. Biomass is a renewable resource that has the potential to replace fossil fuels. One of the valuable biomass products is bio-methanol, which can be used to generate electricity and power for portable applications. This paper discusses the potential of bio-methanol as a renewable resource taking into account the world demand, economic assessment, power density and possible applications. It therefore presents the unique properties of bio-methanol as a potential energy resource. It also discusses the various types of biomass that can be obtained from waste products and the different processes that have been developed for the production of bio-methanol fln addition, it discusses the current problems facing bio-methanol production and the further technological improvements that are needed to support the future energy requirements. Overall, the yield of bio-methanol depends on the type of process used and the associated kinetic parameters of the conversion process. Catalysts have been used in the thermo-chemical and bio-chemical conversion of carbon dioxide into bio-methanol. Several advanced methods have been recently introduced to enhance the production of methanol, but further research is required before these can be used for large-scale bio-methanol production.

Contents

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1. Introduction

Technology enhancements and human development contribute to the continuous increase in the worldwide energy demand [1–3]. There are three categories of energy sources: fossil fuels, renewable and nuclear energy. Fossil fuels, such as coal, petroleum and natural gas, are non-renewable energy sources that will be depleted in the next few years [4–6]. The renewable energy sources include solar, wind, hydroelectric, biomass and geothermal energy, whereas nuclear energy is derived from fission and fusion reactions [6]. Fossil fuel source depletion has increased the need to reduce the consumption of fossil fuels [7–9]. However, the depletion is not the only current concern with fossil fuel use. The environmental degradation caused by burning fossil fuels and the waste products produced have created an imbalance in the atmospheric carbon dioxide (CO_2) levels, which has become the major contributor to global warming [10]. In addition, the municipal solid wastes from human and animal activities have also contributed to the environmental degradation. Therefore, it has been suggested that this waste should be recycled or converted into energy [11–14].

The disposal of agricultural, human and animal waste (solid) that is categorised as biomass material is yet another problem that should be addressed. In addition to its use as a plant fertiliser, animal waste can be converted via a chemical reaction and thus has the potential to be used as a chemical feedstock. The fossil fuel emission during fuel processing has prompted the search for renewable sources that emit zero or low pollution. The use of bio-methanol from biomass is more advantageous than fossil products because of its low pollution emission and raw material availability; furthermore, the characteristics of this alcohol are identical to those of fossil fuel. Hence, biomass is a renewable energy source that can potentially replace fossil fuels [7,15,16]. It is well-known in certain countries, such as Brazil and the US, that bio-methanol from biomass can produce electrical energy [17]. This paper discusses the various types of biomass that can be obtained from waste, the different processes that are available for methanol production and the current problems that are involved in the production of methanol. In essence, this paper will discuss the potential of bio-methanol as a renewable power resource.

2. The potential of methanol as a future renewable energy source

2.1. World demand for methanol

In 2000, approximately 6.2 billion tons of carbon was emitted into the atmosphere as CO_2 and approximately 40% of this was emitted during the production of electricity. A survey from the U.S. Department of Energy revealed that the consumption of electricity, which increases significantly every year, is projected to increase by 44% from 2006 to 2030 [18]. By 2050, road transportation is expected to be the largest contributor to greenhouse emissions. In Europe, the renewable energy target for 2010 was approximately 5.75% of the transport fuels sold, and this target will likely increase to 10% in 2020. If this trend continues, the renewable energy target for the transport fuels sold should reach 27% by 2025. Compared with the gasoline and fossil diesel demands (51% and 22%, respectively), biofuels are expected to constitute 75% of the total demand [19].

Natural gas comprises approximately 80% of the total cost of methanol production in Western European methanol plants [20]. In fact, the total cost of methanol production from CO_2 is 500–600 € t^{-1}; however, the cost of producing methanol from biomass is approximately 300–400 € t^{-1} of methanol [21]. Thus, biomass processing is the most cost-effective of the processes that have been developed for the production of methanol from renewable sources [19]. The production cost of bio-methanol is lower than that of light oil, which is used in power stations [7]. Hasegawa et al. [17] reported that the U.S. and Brazil currently monopolise the biomass processes for bio-ethanol production using grain or the combination of sugar cane and corn. However, because the feedstock (corn) for these bio-ethanol products is a food product, this practice has attracted criticism given the increasing food prices and the global food shortage. Although both methanol and ethanol are liquid hydrocarbons, ethanol is twice as expensive as methanol. However, the location, capacity, mode of operation, operating conditions and the purity grade of the final product are factors that affect the economics of methanol production.

2.2. Economy assessment of methanol

As one of alternative compound, more than 75% of methanol produced by natural gas, synthesis from the syngas. Today, about 90 methanol plants generated with a total annual capacity of more than 50 million tons. Fig. 1 presents the price for production of methanol from fossil resources. The price of methanol is not stable from year 2006 until 2009 but after that, the price is increased until year 2011. Therefore, as demand for the methanol increased, it is expected that the price of methanol will also increase in next future [22].

Adamson et al. claimed that about 3.13 USD GJ^{-1} in year 1990 required for production of methanol via electrolysis process with hydropower feedstock. While for gasification of biomass, plant size

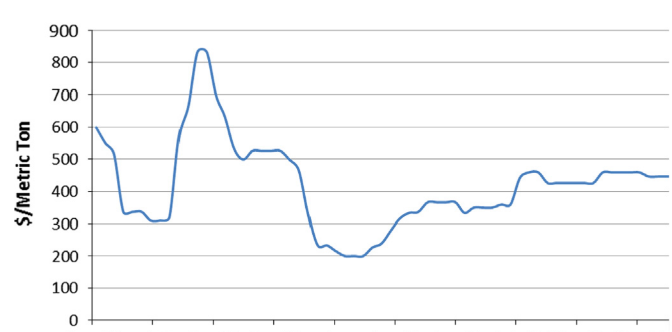


Fig. 1. Methanex non-discounted reference price of methanol (MNDRP) [22].

1650 dry tons/day in 1991 required 9.55–14.10 $\$GJ^{-1}$ of methanol cost and with same plant size, required costing 9.83–14.18 USD GJ^{-1} in year 1993 [21]. Pedersen et al. [22] who studied the production of methanol from biomass by steam reforming (SR) and partial oxidation (POX) of technical and economic assessment in year 2012 claimed that methanol can be produced at a competitive price of 687 USD t^{-1} by farm scale, 419 by large scale of partial oxidation and 453 USD t^{-1} by steam reforming. It shows the highest price of production in farm scale, while the cheapest production price is achieved by the large scale plant via partial oxidation. Even though it required largest annual expenditures, the larger throughput of methanol outweighs this disadvantage.

Kumabe et al. [7] reported that plant size is 91.1 kg dry s^{-1} wood and the wood procurement cost is 7.1 ¥ kg dry^{-1}, the BTL MeOH cost is 12.8 k¥ m^{-3} MeOH, while it is 78 k¥ m^{-3} MeOH when the plant size is 1.16 kg dry s^{-1} wood and the wood procurement cost is 0 ¥ kg dry^{-1}, by biomass to liquid process (gasification). Lundgren et al. [23] investigate the feasibility of an innovative way of producing methanol from off-gases and they proved that integrating methanol production in a steel plant can be made economically feasible and may result in environmental benefits as well as energy efficiency improvements.

2.3. Applications of methanol

As a renewable carbon resource, biomass can be converted from a solid phase into a wide range of chemicals that can be used as liquid fuels (biofuels), such as bio-oil, bio-ethanol, bio-methanol, bio-diesel, liquid hydrocarbons, mixed alcohols, acetic acid and formaldehyde. However, bio-methanol has the most potential as a biofuel for power generation because it is a distributed form of energy production [24]. Moreover, methanol is suitable for additional downstream applications, such as fuel cell-powered vehicles, because it can be easily degraded to carbon dioxide and hydrogen in the presence of steam. Methanol is the simplest organic liquid hydrogen carrier that acts as a hydrogen storage compound. It is also an attractive automotive fuel because of its physical and chemical characteristics. A mixture of methanol and conventional petrol, such as M85 (85% methanol and 15% unleaded gasoline), has enabled the production of methanol-fuelled vehicles without necessitating any major technical modifications to the existing vehicles. Since methanol was introduced in China in 2008, the amount of E85 used in China has included the blending of more than 1 billion US gallons (3,800,000 m^3) of methanol into fuel [25]. In addition to its applications as an automotive fuel and as feedstock for chemical production, methanol can be used for biodiesel production by vegetable oil (triglyceride) transesterification and as a fuel for direct methanol fuel cells without an on-board reformer. Fuel-grade methanol is a clean and efficient alternative fuel for gas turbines in power industry applications [26]. As alternative fuels for motors, methanol, ethanol and DME achieve a similar reduction in carbon dioxide emissions; however, if the amount of heat used in their production is taken into account, the use of methanol and DME results in a higher CO_2 reduction than ethanol [27].

In the transportation sector, methanol is superior to gasoline because it burns at a lower temperature. The low volatility of methanol reduces the risk of an explosion or flash fire. Furthermore, methanol fires can be easily extinguished with water because methanol is less flammable than gasoline. Methanol can also be easily and safely transported in its liquid phase by road, rail, ocean tanker or pipeline, which makes it more advantageous than hydrogen due to the problems associated with hydrogen storage. In addition, methanol has lower volumetric energy content than gasoline, which would require minimal changes to the existing fuel distribution networks. Moreover, methanol has a greater octane number (1 0 7) than gasoline (98) [8,19]; thus, this fuel is an attractive choice for high-compression engine applications given its compression ratio modification, valve timing, low cost and increased power [8]. In addition, methanol has a wider flammability range than petrol (6–36.5 vol% and 1–7.6 vol% for methanol and petrol, respectively); hence, even though petrol rapidly reaches its lower flammability limit, it also rapidly reaches its upper limit [21].The required feedstock for producing formaldehyde, methyl tertiary butyl ether (MTBE), acetic acid, methyl methacrylate and dimethyl terephthalate includes approximately 70% methanol. In addition, methanol is a well-known anti-frost agent, inhibitor and solvent [20].

The rapid growth of chemical technologies and industries that contribute to air and environmental pollution requires some limitations to prevent the excessive emission of carbon dioxide into the atmosphere. A carbon dioxide recycling system that uses carbon dioxide from flue gas and renewable hydrogen from the electrolysis of wind farms was developed to produce methanol. Approximately 0.19 t of bio-methanol can be produced from 1 t of fossil fuel, which could result in a decrease of 0.42 MTon in CO_2 emissions per year; a total of 0.27 t of CO_2 are emitted per ton of methanol at a power energy cost of 0.01 USD kWh^{-1}using an electrolysis system [20]. Naqvi et al. [28] had presented black liquor gasification (BLG) systems for methanol production and reduction of CO_2 as potential technology candidates for the future deployment.

2.4. Power density of methanol

Methanol exhibits more efficient energy storage than compressed hydrogen in terms of weight and volume. Methanol has a higher volumetric energy density (99 gL^{-1}) than liquid hydrogen (71 gL^{-1}) and therefore does not require the use of a cryogenic container that needs to be maintained at a temperature of -253 °C [25]. As the primary fuel in fuel cells, methanol consists of a 6100 kW kg^{-1}energy density, which maximises the operational life-time of the fuel cell in the limited fuel cartridge volume [29]. In addition, a fuel cell that uses methanol as the primary fuel cell achieves an energy output of 480 Wh in a volume of 0.6 L and a run time of 19 h, which signifies a 7.4 WL^{-1} power density and a 289.2 Wh kg^{-1}energy density. A methanol–water mixture that is used indirectly as a polymer-electrolyte membrane fuel produces energy output of 166 Wh with 0.24 L of methanol over 7 h, which corresponds to a power density of 16.9 $WL^{-1}$and an energy density of 112.2 Wh L^{-1} [30]. A Japanese company, Sharp Corporation, achieved a power density of 0.3 Wcc^{-1} in a direct methanol fuel cell (DMFC) that gave efficient power generation in mobile equipment from a small cell volume; this power density is, to date, the highest that has been attained [31]. Hamelinck et al. [32] conducted a technical and economic evaluation of methanol production and found that the overall energy efficiency for bio-methanol production was 55% of the high heating value. A hot gas cleaning process improved the production system performance. An input of 400 MW produced biofuels at US \$ 8–12GJIt^{-1}.

3. The potential of using biomass and waste for bio-methanol production

3.1. Types of bio-mass

Biomass is an organic or carbonaceous material that stores sunlight in the form of chemical energy through photosynthesis. It can be used as an alternative for fossil fuels for several reasons: (1) it is a source of sustainable renewable energy, (2) it is

environmentally friendly, (3) it has significant economic potential and (4) it creates energy security [33]. Biomass is defined according to its purpose and application, which are different depending on the field. There are five categories of biomass: wood fuels derived from natural forest and woodland sources (e.g., sawdust), agricultural residues (e.g., rice husks, straw and manure), energy crops that are grown exclusively for energy production (e.g., corn and palm oil), urban waste (e.g., municipal solid waste and sewage) and refused-derived biomass fuel (e.g., wooden pellets). The classification of these biomass resources is detailed in Fig. 2.

The utilisation of waste biomass is one of the alternatives to overcome the dependence on fossil fuels. Fig. 3 shows the current stocks of worldwide waste biomass which consist of animal, agricultural, forestry and industry types of waste. Among this biomass, cattle manure is the highest biomass residues generated (23 $EJyr^{-1}$) followed by industrial logs (20 $EJyr^{-1}$) [34]. The amounts of animal waste generated conclude that it has high potential in use as renewable energy. There are a number of benefits associated with using these second generation biofuels, which include a reduction in the amount of food supplies that would need to be diverted to fuel production, a more environmentally friendly production with less greenhouse gas (GHG) emissions, more competitive prices and a wide choice of feedstock [35]. The main component of biomass, cellulosic, is an important component

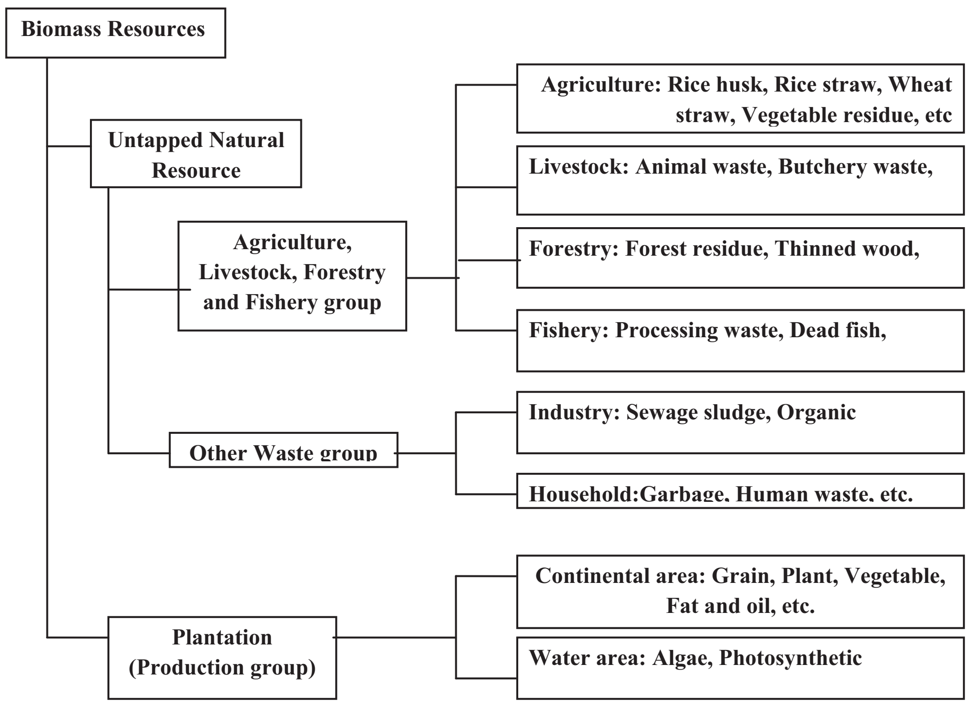


Fig. 2. Biomass resources categorisation [33].

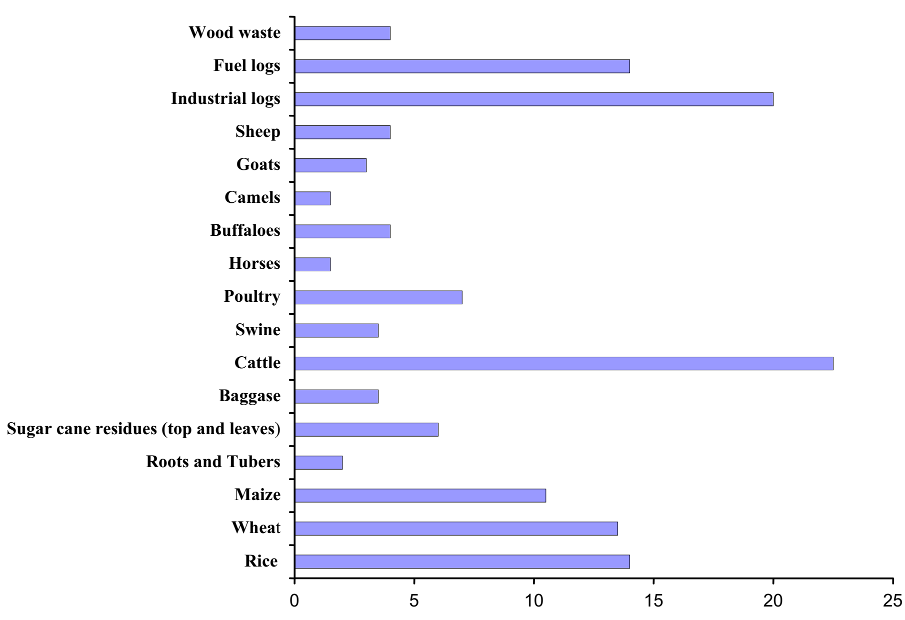


Fig. 3. Amount of biomass residue in the world [36].

in the production of methanol via pyrolysis. The cellulosic biomass, which primarily contains cellulose, hemicellulose, lignin and small amounts of proteins, lipids and ash, can be decomposed to produce a variety of chemical feed stocks, such as methane, methanol, ethanol, acetone, acid acetyl and biofuels [36,37]. Methanol is produced from the breakdown of methyl esters or the combination of ether with the methoxyl groups of uronic acid, which is produced by the decomposition of pectin-like plant material [4]. Xu et al. [38] had presented a novel approach for high efficient conversion of the CO_2-rich bio-syngas into the CO-rich bio-syngas carried out using biomass char and Ni/Al_2O_3 catalyst, which was successfully applied for production of bio-methanol from bio-oil.

3.1.1. *Agricultural waste*

Agricultural waste, which refers to the residue produced in fields or on farms during harvesting and other activities, includes rice husks, rice straw, wheat straw, vegetable residue and other sources. Lignocellulose materials from agriculture and forest management, which have the largest sources of hexose (C-6) and pentose (C-5) sugars, have the potential to be used for the production of biofuels, chemicals and other by-products [39]. The greatest contribution to biomass energy is from agricultural waste, which comprises 64% of the total energy demand [40]. Many developing countries have a wide variety of agricultural residues in abundant quantities [41].

Reno et al. [41] claimed that sugar cane bagasse and corncobs have the potential to produce alcohol components. Nakagawa et al. [42] also tested various types of agricultural waste biomass, such as bran, straw, and husks from rice and found that rice bran produced high methanol yields (55% by weight), whereas rice straw and husks exhibited methanol yields of 36 and 39% by weight, respectively. Chia [43] used rice husks, sugar cane bagasse, corncobs and nutshell samples to examine the presence of alcohol and other components and proved that sugar cane bagasse and corncob contain 5.93% and 0.67% bio-methanol, respectively.

3.1.2. *Forestry waste*

The horticultural waste biomass includes tree trunks, twigs and leaves and is a potential source of cellulosic feedstock. A recent study estimated that a city of one million people could produce enough organic waste (1,300 t per day) to produce 430,000 L of bio-ethanol per day, which could meet the needs of approximately 58,000 Americans, 360,000 French or 2.6 million Chinese at the current per capita fuel use rates [44]. A number of research studies have used woody-based biomass for the production of methanol, including Gullu et al. [6], Kumabe et al. [7], Hasegwa et al. [17] and Dong et al. [45], who proved the presence of methanol in hazelnut shells, spruce wood, beech wood, softwood, and hardwood. Nakagawa et al. [42] also tested various types of biomass resources, such as sawdust and bark from Japanese cedars, chipped Japanese larch, bamboo, salix, cut wood waste from demolition sites and sorghum and showed that these lignocellulose sources (wood materials) produced high methanol yields (55% by weight).

3.1.3. *Livestock and poultry waste*

According to a recent study jointly sponsored by the United States Department of Agriculture (USDA) and the United States Department of Energy (US DOE), the agricultural lands in the United States currently have 35 million dry tons of sustainable biomass/manure feedstock, which comprises 18% of the total available sustainable biomass from these lands [46]. The use of animal manure as a biomass source would allow farmers to take advantage of new markets for what is traditionally a waste product. There are biological or thermo-chemical processes that can be used to convert animal manure feedstock to multiple value-added renewable energy products that can supply heating and power needs or serve as transportation fuels [47]. In the United States, biomass, including animal waste, supplies 15 times more energy than wind and solar power combined and has the potential to supply much more [33].

In addition, the conversion of poultry litter into power is an important milestone in the development of biowaste energy resources. Poultry litter contains organic matter that can be converted into bio-energy using certain processing technologies. One of the most common approaches for poultry excrement, which is managed by water flushing, is anaerobic digestion; this process yields biogas, which is a gas mixture that contains varying concentrations of combustible methane. Currently, there is a 55-megawatt power plant predominantly utilising poultry litter that is operated by Fibrowatt in Minnesota. The plant has the capacity to utilise 500,000 t of poultry litter annually, although it is currently operating below this capacity due to environmental regulations [48]. Weimer et al. [49] proved that the waste of other herbivore animals, such as cow and goat, the mixture of chicken waste and wood and the mixture of chicken waste and sand, can also be used in the production of methanol. Adawiyah [50] developed a small-scale bio-methanol pyrolysis reactor and used a number of biomass sources, including cow and goat waste, a chicken waste and wood mixture, a chicken waste and sand mixture, and palm waste. The results showed that the highest levels of bio-methanol and bio-ethanol were generated from the pyrolysis of the mixture of chicken waste and wood (1.25%) and the mixture of chicken waste and sand (0.028%), respectively.

3.1.4. *Fishery waste*

The Food and Agriculture Organization of the United Nations reported that world fish production in 2006 was 141.6 million tons, and approximately 50% (70.8 million tons) of the total fish material processed became waste with oil contents that varied from 40% to 65% [51]. Most current technologies that use fish industry waste are not economically attractive, and the use of sanitary landfills and effluent treatment ponds in these processes are not recommended because of the unpleasant odour produced. Therefore, the use of a bio-refinery is potential methods to reduce the amount of fish waste and simultaneously produce biofuels, chemicals and other products. Wiggers et al. [52] studied the potential of using fish oil waste in a continuous pyrolysis pilot plant and obtained a bio-oil yield of 72–73%. However, although fish waste was proven to have potential in the production of bio-oil, the production of methanol from fishery waste has not been studied.

3.1.5. *Sewage sludge*

There is an increasing amount of chemical sewage sludge produced by industrial plants and consumers; this sludge includes solid waste and the carbon dioxide, carbon monoxide, hydrogen and methane gases that are released into the air. This is therefore an increasing source of biomass that can potentially be used for the production of methanol. Caballero et al. [53] proved the potential of using sewage sludge in the production of methanol and Ptasinski et al. [20] carried out an exergy analysis of methanol production from sewage sludge.

4. Bio-methanol production

There are several conventional and new processes for the production of bio-methanol, such as pyrolysis, gasification, bio-synthesis, electrolysis and photo electrochemical processes. Pyrolysis technology is more suitable for the large-scale production of methanol for diesel engines and gas turbine applications, whereas

the cost-effective gasification processes are preferred for the production of gaseous fuel. Biosynthesis processes, which use resources such as methane and carbon dioxide to produce methanol, function as conversion processes that use organic waste, such as municipal solid waste, sewage sludge, and primary and secondary agriculture waste, to generate a gaseous fuel. However, new techniques, such as photo electrochemical (PEC) and electrolysis, have been proven to have potential for the production of bio-methanol at a lab scale but require further research prior to their use in large-scale production.

4.1. Pyrolysis

The first synthetic process that was introduced by Gullu et al. [6] in 1927 used a pyrolytic reactor to produce bio-methanol from the catalysed reaction of hydrogen and carbon monoxide under high temperature and pressure. The traditional pyrolysis process produced only 6 gallons of bio-methanol/ton of feed, whereas this synthetic pyrolysis process exhibited better results, with a yield of 100 gallons bio-methanol/ton of feed, or 185 kg of bio-methanol per metric ton of solid waste. Gullu et al. [6] tested several feedstocks, such as hazelnut shells, spruce wood, beech wood, softwood, hardwood and corncobs, as biomass samples and found that hazelnut shells yielded the highest amount of bio-methanol($7.8 \pm 0.5\%$), followed by hardwood ($1.7 \pm 0.2\%$) and ash ($1.0 \pm 0.1\%$).

Ishikawa et al. [54] also used pyrolysis to produce bio-methanol from carbon monoxide and hydrogen that was obtained from biomass sources. Caballero et al. [53] studied the production of bio-methanol from different chemical sewage sludge compositions by pyrolysis with an additional secondary reactor. In addition, these researchers proved that the pyrolysis process produces a liquid product phase that does not harm the environment. Demirbas [55] studied the production of bio-methanol from beech wood using non-alkaline and alkaline pyrolysis processes in an electrical heated tubular furnace and measured yields of 6.44 and 8.75% of methanol, respectively.

Campo et al. [56] conducted a research to study the combined production and purification of hydrogen using redox processes departing from biomass fast pyrolysis oils (bio-oils). While Valle et al. [57] carried out using different techniques on the nature of the coke deposited on a HZSM-5 catalyst modified with Ni in the transformation of the crude bio-oil obtained by flash pyrolysis of lignocellulose biomass (pine sawdust) into hydrocarbons. Later Hu et al. [58] investigated on acid-treatment of the bio-oil from the pyrolysis of mallee leaves in methanol over a solid acid catalyst Amberlyst 70 and this study proves that this treatment improved the quality of the bio-oil. Kanauji et al. [59] presented a review on outcomes of important research related to chemical analysis of bio-oils summarizing the role of prominent analytical techniques in the chemical characterisation of bio-oils.

4.2. Gasification

Galindo et al. [26] studied the utilisation of renewable hydrogen in bio-methanol production using two methods, the syngas production from biomass gasification and the carbon dioxide hydrogenation from flue gas (coal fired power stations), which exhibited energy conversion efficiencies of 25–44% biomass and 17–23% carbon dioxide. Gullu et al. [6] determined that syngas contains hydrogen (30–40% by weight), carbon monoxide (20–30%), methane (10–15%), carbon dioxide (15–20%), nitrogen (0.7–1.1%) and water (5.5–6.6%). This study suggested using a catalyst, such as a reduced nickel oxide (NiO)-based preparation, a reduced Cuprum/zinc oxide (Cu/ZnO) shift preparation, Cuprum/silicon oxide (Cu/SiO_2), palladium/silicon oxide (Pd/SiO_2) or palladium/zinc oxide (Pd/ZnO), to facilitate the production of bio-methanol from syngas.

Kumabe et al. [7] produced syngas, H_2 and CO from woody biomass and obtained a gasification carbon conversion of 95%. Compressed syngas was later introduced and used to produce bio-methanol in a MeOH synthesiser. Chmielniak et al. [60] used a combination of coal and biomass as the input in a gasification conversion to produce bio-methanol. These researchers claimed that the gasification process using this combination yielded a more cost-effective production, better operational stability and optimal thermal efficiency. Moreover, this coal-gasification technology decreases the impact of methanol production on the environment. The coal sample can cover a power shortfall and can be a feasible process in a relatively short period of time on a large scale. Dong et al. [46] proposed the use of a hynol process for methanol production that consists of hydrogasification, steam reformation and methanol synthesis. This process was proposed with an energy recovery design that minimises heat loss while increasing thermal efficiency. Approximately 41% of the carbon dioxide emissions would be reduced if methanol produced from a hynol process was used to replace conventional gasoline fuel. Furthermore, these researchers claimed that the total capital investment for a hynol plant is lower than that for a conventional gasification plant.

Hasegawa et al. [17] adopted a gasification process using ground woodchips (1–2 mm diameter) as the input, a temperature of 800–1000 °C, a conventional Cu/ZnO-based catalyst, oxygen and steam for the synthesis of bio-methanol. Xu et al. [61] used biomass char and a Ni/Al_2O_3 catalyst to convert CO_2-rich bio-syngas to CO-rich bio-syngas, which can be successfully used to produce bio-methanol. The maximum bio-methanol yield was 1.32 kg(kg catalyst h)$^{-1}$with a selectivity of 99% because the bio-gas process conditions were improved. Ricketts et al. [62] proved that bio-methanol can be produced by the partial oxidation of biomass into syngas and a subsequent catalytic conversion process. The syngas produced from biomass in a gasifier had a heating value in the range of 75.6–100.8 kcal scf^{-1} (HHV) [6]. While Ng and Sadhukhan [63] developed a process to process material and heat integration strategies for bio-oil integrated gasification and methanol synthesis (BOIG-MeOH) systems to assess their technological and economic feasibility.

4.3. Biosynthesis

No biological organism is currently known to reduce carbon dioxide to produce methanol. However, the methanotrophic bacteria *Methylosinus trichosporium* IMV 3011 was used as a bio-catalyst in the production of methanol from greenhouse gases (carbon dioxide and methane) without requiring the addition of hydrogen [64]. Duan et al. [65] and Lee et al. [66] used *Methylosinus trichosporium* OB3b to produce methanol by the oxidation of methane to methanol with a high concentration of Cu^{2+}, whereas Duan et al. [65] conducted the biotransformation of oxygen and methane in a membrane aerated reactor to produce 0.95 gL^{-1} of methanol. These researchers used a high cell density process with *Methylosinus trichosporium* OB3b and a high concentration of phosphate buffer. In addition, Takeguchi et al. [67] used *Methylosinus trichosporium* OB3b for methanol production and concluded that changes in the cell density, reaction temperature, pH 7.0 and the concentrations of sodium formate, phosphate buffer and cyclopropanol were essential in the optimisation of the conversion rate of methanol. Kim et al. [68] developed a compulsory circulation diffusion system for cell cultivation, which is shown in Fig. 4, that utilises a mixture of methane and air to produce 2.17 μmol methanol (hmg dry cell weight)$^{-1}$.

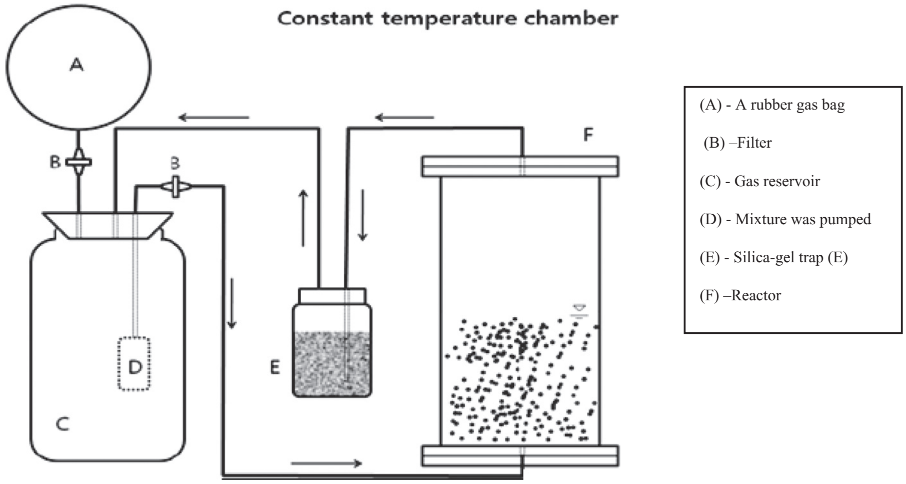


Fig. 4. Schematic diagram of lab-scale compulsory circulation diffusion system for methanol production [68].

4.4. Methane

Even though methane is not a harmful gas, such as carbon dioxide, approximately 5000 trillion cubic feet of methane was emitted in gas field processes. Holmen [69] stated that the methane produced from biomass feedstock can be directly converted into methanol by a heterogeneous catalyst. Although homogeneous catalysis was suggested for the activation of methane at a low temperature, it yields a product that is more reactive than methane.

Wang et al. [70] studied the direct conversion of methane to methanol in the Argon 50 W radio-frequency plasma system and showed that approximately 19.1% of methane was converted into 1.12% methanol at a CH_4/O_2ratio of 40/60. This high conversion of CH_4 is the result of the large plasma discharge area, which causes a long residence time. However, although the overall conversion was high, the yield of methanol was still low because it was decomposed to CO and CO_2. Yao et al. [71] studied a methane selective oxidation process to produce methanol using non-thermal pulsed plasma and achieved a 1.9% methane conversion with 47% methanol selectivity, which is more sensitive to the discharge input power compared to the oxygen concentration and discharge length. Okumoto [72] studied the partial oxidation of methane using the pulsed discharge plasma method at room temperature and atmospheric pressure and found that a number of products, such as ethylene (C_2H_4), ethane (C_2 H_6), formaldehyde (HCHO), hydrogen (H_2), water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2), were produced in addition to methanol. This experiment showed that both methanol and formaldehyde exhibited an optimal specific input energy (SIE) of 360 JL^{-1} and a 50 vol% argon concentration. The combination of methanol and formaldehyde has a maximum production of 0.7 $\mu molJ^{-1}$ with a selectivity of 64 mol%. Mahajan [73] studied the conversion of natural gas and carbon monoxide into methanol with a soluble transition metal complex as a single-site catalyst. The results showed that the nickel complexes, which were activated by alkoxide, were able to reduce CO at a temperature and pressure range of 80–130 °C and 2000–5000 kPa, respectively, to obtain 90–95% methanol selectivity.

Lee [74] recently reported that methane could be oxidised to methanol by the proton conductor $Sn_{0.9}In_{0.1}P_2O_7$ and the highly active Pd–Au–Cu/Ct. In addition, methane will oxidise to methanol in the presence of a Pt–Au–Cu/C electrode, water and oxygen at a temperature of 300 °C or higher. Certain reactions take place at the anode electrode, which is where the water is oxidised, whereas the cathode electrode reduces oxygen to produce methanol. The same reactions are also generated with a $Sn_{0.9}In_{0.1}P_2O_7$+Pd–Au–Cu/C mixed catalyst. There are two factors that are important in the characterisation of the synthesis of methanol using a mixed catalyst. First, the yield was higher by one order of magnitude than what was obtained with an electrochemical cell. Second, the high selectivity in the temperature range of 250–350 °C should be evaluated. Li et al. [75] investigated the effect of different catalysts on the conversion of methane into methanol and found that the combination of nano-gold (Au/SiO_2) and IL promotes the reactivity of gold with high selectivity. In addition, this catalytic system has no environmental impact in the absence of concentrated sulphuric acid and heavy-metal catalysts. Rivarolo et al. [76] performed a thermo-economic analysis regarding large scale hydro-methane and methanol production from renewable sources (biomass and renewable electricity).

4.5. Carbon dioxide and carbon monoxide

Meyer et al. [77] stated that the Carnol system is a feasible and economical technique that produces methanol and reduces the flue carbon dioxide that reacts with hydrogen. Approximately 100% and 65% of the carbon dioxide emissions can be reduced with methanol production and the overall system, respectively. In addition, a study by Sahibzada et al. [78] demonstrated that carbon monoxide, which is abundant in the atmosphere, can also be converted to methanol. Xu et al. [61] used formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase as catalysts for the reduction of CO_2 and obtained methanol yields of 98.8%, 71.3% and 98.1%, respectively.

Shen et al. [79] studied the catalytic activity of Ceria and other copper catalysts in the synthesis of methanol from carbon monoxide and hydrogen and found that carbon monoxide and hydrogen reacted with Cu/CeO_2 catalysts at 195 °C to form methanol. The results indicated that using Cu/CeO_2as the catalyst yielded the highest amount of methanol (43.9 mol $dm^{-3}h^{-1}$). Yang et al. [80] obtained methanol from a 20-h reaction of CO, CO_2 and H_2 at 443 K and 5 MPa using $Cu/ZnO/Al_2O_3$as the catalyst with a 5% Cu loading. The highest amount of methanol was produced by a Zn:Cu molar ratio of 1:1, which resulted in a productivity increase of 112.3%. The productivity was decreased by 20.0% when the Zn:Cu ratio was changed from 1:1 to 2:1.

Ma et al. [81] studied the catalytic activity of Cu/ZnO, which has a large BET surface area, large pore volume, fine particle size and uniformly distributed metal oxide crystallites, and obtained a 7.1% yield of methanol with 38.4% selectivity and an 18.5% CO_2 conversion). Le [82] studied the effect on surface chemistry and reaction behaviour of copper oxide in the electrochemical reduction of CO_2 to methanol. The results show that the methanol yield is dynamic and could be increased to 87 μmol cm^{-2} h^{-1} with Faradaic efficiencies greater than 100%; during this process, the copper oxide was reduced to metallic Cu. Soltanieh et al. [83] presented an integrated system for co-production of electricity and methanol as well as decreasing the CO_2 emission into the atmosphere. They also develop a renewable energy sources for carbon capture. In this research, methanol synthesis unit through captured CO_2 from fossil fuel power plant and produced H_2 from water electrolysis unit by wind renewable energy.

4.6. Photo-electrochemical (PEC) processes

In addition to hydrogen, methanol is one of the outputs of a photo electrochemical cell that uses methane from natural gas or biomass [84]. The reaction of methane and water produced methanol, hydrogen and acetic acid at 94 °C with a doped semiconductor photo-catalyst. This conversion was augmented by the addition of hydrogen peroxide and resulted in the production of a hydroxyl radical as an intermediate [85]. Halmon [86] proved that methanol can be accumulated from carbon dioxide in aqueous form using photochemical cells with semiconductor surfaces, such as *p*-type gallium phosphide, in a photo-assisted electrolytic reaction. Moreover, this PEC conversion of visible light to a chemical has a relatively high efficiency. Unfortunately, the efficiency of PEC cells is still low and semiconductor photo electrodes exhibit poor stability in the reaction of water by solar irradiation.

Ganesh [87] studied the reduction of carbon dioxide to methanol with a molybdenum cathode and obtained a methanol selectivity of 80% with a 100% faradic efficiency. The use of p-GaP as the catalyst in the photo electrochemical cell resulted in a conversion yield of CO_2 of approximately 95% with a 100% methanol selectivity. However, the stability of the semiconductor should be tested to determine the feasibility of using this process commercially. Jeffrey et al. [88] studied the photo reduction of CO_2 to methanol using a TiO_2 photo catalyst, an Hg lamp (365 nm), and a steady state optical fibre photo reactor and found that the yield of methanol increased with increasing UV irradiative intensity.

4.7. Electrolysis

Weimer et al. [50] suggest that pure oxygen, which is formed from the electrolysis of biomass gasification to produce syngas, can react with equivalent volumes of hydrogen and carbon monoxide to produce methanol. Sahibzada et al. [78] discovered that methanol can be synthesised by the reaction of a small amount of water ($<2\%$) with CO and H_2. These researchers also isotope-labelled the H and O in water prior to its reaction with a hydroxyl group and carbon monoxide to produce methanol.

Katayama [89] introduced the production of methanol by a combination of electrolysis and water using renewable solar energy and a fossil fuel (coal) as the raw material. The function of renewable energy is to provide the electricity required for the electrolytic separation of water to become H_2 and O_2. One mole of water can be produced from one mole of H_2 and 0.5 mol of O_2using renewable electric energy. Lee et al. [90] showed that methanol can be produced by the direct oxidation of methane at a low temperature in a fuel cell reactor. The use of a Pt/C anode at a temperature between 50 and 250 °C failed to produce methanol; however, a V_2O_5/SnO_2 anode at 100 °C produced methanol with a selectivity between 61.4% and 88.4%.

5. Kinetic parameters

Table 1 summarises the kinetic parameters in the production of bio-methanol using different processes and raw materials. As shown, the thermal and bio-synthesis processes usually use biomass, methane, syngas, carbon dioxide or hydrogen as the feedstock for methanol production. The pyrolysis and gasification conversion studied by Gullu et al. [6], Kumabe et al. [7], Hasegawa et al. [17], Xu et al. [61], Galindo et al. [26], Dong et al. [46], Nakagawa et al. [43], Van Ren et al. [56] and Chmielnik et al. [60] produce a large amount of methanol in the industrial scale; therefore, the use of biomass feed in this type of conversion technology has greatly improved since 1927 [6]. Comparison of bio-methanol yield by these two conversions show that gasification produced higher amount of bio-methanol than pyrolysis. According to Gullu et al. [6] data, about 2% until 18.5% of bio-methanol produced by biomass over total feedstock which can be considered less compare to gasification that able to obtain from 22.36% [56] until more than 100% of bio-methanol over total of feedstock [26]. Beside biomass, coal, carbon dioxide, methane, natural gas and steam also used in production of bio-methanol via gasification [46,50]. However, there are several new processes that have been introduced, such as biosynthetic, electrolytic and photochemical processes [91]. These processes have been proven to produce methanol in a lab scale but require further development for large-scale production. These new processes were able to produce bio-methanol in small amount compare to pyrolysis and gasification conversion.

6. Current problems with bio-methanol production

The syngas that is produced from gasification processes is considered suitable for bio-methanol production. However, it requires large amounts of biomass for large-scale bio-methanol production. In addition, the biomass resources should be non-edible to ensure that these do not compete with food crops. In addition, Sayah et al. [29] reports that, in 2030, the price of methane will likely be 5000 USD t^{-1} and that the cost of the conventional methanol synthesis will likely be 150 USD t^{-1} methanol. The green methanol synthesised from flue gas and wind hydrogen will require a material cost increase of 1.71% that can be decreased to 1.11% through the use of an integrated system, which can produce 0.19 t of green methanol for each ton of fossil-based methanol, thereby reducing the methane in the feed gas. Furthermore, an integrated system can decrease the annual CO_2 emissions by 0.42 M tons.

Reno et al. [41] reported that the ratio of fuel energy to fossil energy (Efossil) consumed during the methanol production process (FER) is higher with the use of sugarcane bagasse than with coal or natural gas. Therefore, the combination of sugarcane bagasse and trash might be used for methanol synthesis. The BIG-GT (Biomass Integrated Combined Cycle Gasification-Gas Turbine) technology can produce steam that can be supplied to distilleries and methanol plants. One disadvantage of gasification and methanol synthesis is the emission of pollutants that negatively impact the environment, such as ash, tar, particulates, and carbon dioxide. Hence, a more advanced gas cleaning system, such as through the use of metal filters, candle filters, sorbents, catalytic tar crackers, or the use of a CO_2 capture system, might minimise the impact of emissions on the environment. Although gasification and methanol synthesis have been extensively researched, only a

Table 1
Summary of kinetics parameter of methanol production.

References	Conversion process	Raw materials	Kinetics parameter involved
Gullu et al. [6]	Pyrolysis	Solid waste	185 kg of bio-methanol per metric ton of solid waste
Gullu et al. [6]	Pyrolysis	Hazelnut shells	Bio-methanol yield 7.8 ± 0.5% of dry and ash weight from 10 to 18% charred residues
Gullu et al. [6]	Destructive distillation	Wood	6 gallons bio-methanol (2%) per ton of wood
Gullu et al. [6]	Gasification	Biomass	100 gallons of bio-methanol per ton of biomass
Galindo et al. [26]	Gasification	Biomass	12.21 kton/year of methanol from 10.10 dry kton/year of biomass
Galindo et al. [26]	Gasification	Biomass	17.60 kton/year of methanol from 14.40 dry kton/ year of biomass
Kumabe et al. [7]	Gasification (biomass to liquid-MeOH)	Wood	47.7 (wt%) of bio-methanol from (400 tdry/d) wood
Dong et al. [45]	Gasification	(Biomass + steam + methane	199.2 kg bio-methanol from 100 kg biomass + 1.2 kg steam/biomass + 0.5 kg methane/kg biomass)
Dong et al. [45]	Hynol gasification	Wood + natural gas	101.5 MM gallon/year bio-methanol (38,494 kg/h) from 2000 short ton per day of wood (75,598 kg/h)
Hasegawa et al. [17]	NEDO (gasification)	Wood	510 L methanol from one metric ton of wood (15% moisture content)
Xu et al. [61]	Gasification	Conditioning bio-syngas + biomass char of rice husk	1.32 kg/ (kg catalyst h) of bio-methanol from 120 kg/h oil rice husk
Weimer et al. [50]	Gasification + electrolysis	Carbon dioxide	200 t rnethanol/d from 3,125 × 10^6 mol CO_2/d
Nakagawa et al. [42]	Gasification	Biomass: agricultural waste	38–50% by weight (methanol/dry weight raw material) of bio-methanol from 100 kg/day dry biomass to be process
Van Ren et al. [56]	Gasification	Wood	Methanol of 18.237 t h^{-1} from wood 81.540 t h^{-1}
Chmielnik et al. [60]	Co-gasification	Raw gas from coal) + biomass	132.5 thousand m^3 of methanol from 1000 t/day of raw gas + biomass
Sahibzada et al. [78]	Electrolysis	CO_2/H_2 (differential conversion)	0.44 (mol h^{-1} g^{-1} Cu) rate of methanol from Cu/Zn/Al^{-1} of catalyst, CO_2/H_2 (698 mol h^{-1} g^{-1} Cu) yield
		20:80 CO_2/H_2	0.45 (mol h^{-1} g^{-1} Cu) rate of methanol from 0.09 Pd/Cu/Zn/Al, CO_2/H_2 (698 mol h^{-1} g^{-1} Cu)
Sahibzada et al. [78]	Hydrogenation	CO_2/H_2+H_2O (differential conversion)	0.043 (mol h^{-1} g^{-1} Cu) rate of methanol from Cu/Zn/Al^{-1} of catalyst + CO_2/H_2 (698 mol h^{-1} g^{-1} Cu) + H_2O (18.5 mol h^{-1} g^{-1} Cu) 0.057 (mol h^{-1} g^{-1} Cu) rate of methanol from 0.09 Pd/Cu/Zn/Al + CO_2/H_2 (698 mol h^{-1} g^{-1} Cu) + H_2O (18.5 mol h^{-1} g^{-1} Cu)
Taylor et al. [91]	Photocatalytic + thermochemical	Methane	i. No catalyst: 0.13 mL/min (flow) of methane produced 0.04 mL/min of methanol (by 90% of methane conversion) ii. With hydrogen peroxide as catalyst: 0.20 mL/min (flow) of methane produced 0.17 mL/min methanol

small number of studies have discussed the separation processes, particularly the separation of gas and solids, that would be required to reduce the environmental impact of both methods.

Chia [44] determined the presence of alcohol and other components in rice husks, sugar cane bagasse, corncobs and nutshell samples and found that only sugar cane bagasse and corncobs contained bio-methanol (5.93% and 0.67%). However, this research only focused on the liquid yield and suggested that the gas released should be collected and converted into a liquid phase. Due to low boiling point of methanol, some of the methanol may evaporate. Therefore, the conversion of bio-gas into a liquid phase should be considered in future research studies and a condensation process can be used to analyse the components in the bio-gas. However the main problem in the extraction process of methanol is due to the small amount of bio-oil obtained. Large amount of biomass and system optimisation are significant for this process in order to increase the production of bio-methanol.

Van Rens [56] showed a conversion efficiency of 54% in the production of bio-methanol from biomass using a gasification process with an exergetic efficiency of 55%. Clausen et al. [92] showed a 68–72% exergy efficiency using a gasification process in a methanol plant. However, the costs of the plant are approximately 11.8–14.6 $EGJex^{-1}$, which is comparable with the secondary production of ethanol (12.0 E $GJex^{-1}$), but current commercial methanol syntheses are more cost-effective (7.1 $EGJex^{-1}$).

Dixon et al. [93] reported that methanol is mainly (97%) used by microbes for obtaining energy in oligotrophic regions (tropical North East Atlantic); in shelf and coastal areas, however, approximately 20–50% of methanol can be used for cell growth. A methanol concentration of less than 0.2 $\mu g\, l^{-1}$ contributes to the bacterial carbon demand; however, the low air to sea methanol flux estimate of 7.2^{-13} $\mu mol\, m^{-2}\, d^{-1}$ suggests that the atmosphere is not a major methanol source. Therefore, it is necessary to determine a process that uses the in situ oceanic methanol source in these latitudes, which is the sunlight-driven decomposition of organic matter.

Nazimek et al. [94] stated that CO_2 is a thermodynamically stable molecule and that its reduction is therefore highly endothermic. The typical production of methanol from syngas with a catalyst requires pure syngas, which is difficult to obtain from a mixture of gases (CO, CO_2, and H_2). However, the productions of methanol from CO_2 do not require the production of pure syngas. Water can be electrolysed with the photo radiation of hydrogen produced from CO_2. For each *k*-mole of methanol produced from CO_2 and H_2O, 586 MJ of energy, 300 bars of pressure and a temperature 873 K are required. The process, which was conducted in the liquid phase, is not thermodynamically feasible because equilibrium cannot be reached. Therefore, the reduction of CO_2 with photo catalysis is a promising field that should be explored. CO_2 can be converted into other chemicals through irradiation with UV light at ambient temperature. However, more detailed research with controlled reactions is required to enhance the production of methanol. Olah et al. [95] claimed that one of the advantages of the electrochemical process is the generation of CO and H_2 with no impurities (sulphur) that could deactivate the catalyst. However, further research is required to demonstrate the potential of this system in the large scale production of bio-methanol.

7. Conclusion

The components of various biomass sources contribute to renewable energy, or bio-energy. All of the reviews and

investigations on biomass show that it can be used to produce methanol through certain conversion processes and technologies; therefore, biomass has the potential to replace fossil fuels. Methanol can be produced through a number of thermochemical processes, including pyrolysis, gasification and liquefaction, depending on the types of products sought. The biochemical pathway can be divided into three categories: anaerobic digestion, alcoholic fermentation and agrochemical synthesis of methanol. The component in the samples studied primarily contain carbon dioxide, carbon monoxide, carbon, methane and water in either a gas, liquid or solid phase. Therefore, methanol can be produced from additional reactions of decomposed biomass material. The parameters for the different reactions, such as temperature, heating rate, particle size, type of conversion process and residence time, affect the yield. In addition, the high efficiency yields that can be obtained using certain catalysts depend on the type of biomass feedstock that is used.

In conclusion, the design and heat integration of the system are essential. Therefore, more studies in process systems engineering, including heat integration, are needed to develop a more efficient integrated system that can reduce the exergy efficiency and improve the techno-economics associated with the production of methanol. A scale-up of the process design is also important, particularly for the new advanced processes that have recently been introduced for the production of bio-methanol; in these cases, although the lab-scale methanol production has exhibited a high efficiency, it is necessary to ensure that this efficiency is feasible in a large-scale production. An improvement in the electrolysis process and the renewable electricity efficiency, as well as the cost-effective availability of hydrogen at USD 1–2 kg^{-1}, would lead to improvements in methanol synthesis.

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